



Initial responses of carbonate-rich shelf sediments to rising atmospheric $p\text{CO}_2$: Role of high Mg-calcites

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Carbonate rich sediments at shallow ocean depths (<200 m) represent a major CaCO_3 reservoir that can rapidly react to decreasing saturation state of seawater with respect to carbonate minerals produced by rising atmospheric $p\text{CO}_2$. Aragonite is usually the most abundant carbonate mineral in these sediments. The second most abundant carbonate mineral is high magnesian calcite whose solubility can exceed that of aragonite making it the “first responder” to a decreasing saturation state in seawater.

For the naturally occurring biogenic Mg-calcites, dissolution experiments have been used to predict their “stoichiometric solubilities” as a function of mol% MgCO_3 . However, the only valid relationship that one can provisionally use for the metastable stabilities of magnesian calcite based on composition is that for the synthetically produced phases where metastable equilibrium has been achieved from both under- and over-saturation. Biogenic Mg-calcites exhibit a large offset in solubility from that of abiotic Mg-calcite and can also exhibit a significant range of solubilities for biogenic Mg-calcites of similar Mg content. These differences probably reflect to some extent differences in minor element compositions and carbonate anion and cation disordering.

In spite of the uncertainties associated with the solubility vs. magnesium content trend of biogenic Mg-calcites, a simple thermodynamic/kinetic model was used to predict the initial responses of these phases to rising $p\text{CO}_2$ adopting a range of solubilities related to their MgCO_3 content based on experimental results. The results suggest that Mg-calcite minerals will sequentially dissolve following a pathway determined by their solubilities, progressively leading to removal of the more soluble phases until the least soluble phases remain. The modeled timing of the undersaturation of sea-

water with respect to a certain phase composition, and hence its dissolution, varies greatly because of the uncertainty associated with the Mg-calcite mineral solubilities. However, the modeled trend agrees well with laboratory experiments in which various carbonate phase compositions were exposed to different $p\text{CO}_2$ levels. Furthermore, observations from Devil's Hole, Bermuda, show sequential dissolution of metastable carbonate minerals below the seasonal thermocline during summer, where decomposition of organic matter produces $p\text{CO}_2$ levels significantly higher than what is observed in today's atmosphere. As atmospheric CO_2 concentrations continue to increase owing to human activities, the average mineral composition of contemporary carbonate sediments may change, favoring carbonate minerals with a lower magnesium content and consequently lower solubility. Furthermore, the magnesium content of skeletal hard parts produced by calcifying organisms, which may contain more than 20 mol% MgCO_3 , may also decrease owing to decreasing surface water carbonate saturation state. The CO_2 uptake associated with the dissolution of the metastable carbonate phases in the shallow ocean over the next 100 years will probably be in the range of a few percent of the atmospheric increase.